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Research paper

Mitigating CO_2 Emission Via Catalytic Conversion to Methane : a Feasibility Study of Metal Oxide Supported Nickel Based Catalysts

A. Abu Seman[*], N. H. Berahim and M.G.M. Noh

PETRONAS Research Sdn Bhd, Lot 3288 & 3289, Off Jalan Ayer Itam, Kawasan Institusi Bangi, 43000 Kajang, Selangor, Malaysia
Corresponding author E-mail: akbar_seman@petronas.com.my

Abstract

Exploration and production of sour gas field raise the need for CO_2 management to minimize the adverse effect of green house gas venting to the environment. It is a fine balance between the sunken value of CO_2 reinjection and value creation in CO_2 conversion to value product, essential in ensuring project's economic viability. Conversion to methane is selected due to the ease of integration with current process facility. Catalytic conversion of CO_2 to methane are reported here over metal oxides (Al_2O_3, ZrO_2 and La_2O_3) supported Nickel base catalysts over a range of temperature and GHSV with fixed H_2/CO_2 molar ratio. The catalysts were prepared by wet impregnation technique at room temperature. It was then characterized with X-Ray Diffraction (XRD), Brunauer–Emmett–Teller (BET), Temperature Programmed Reduction (TPR) and Temperature Programmed Desorption (TPD). All catalyst systems showed trend of decreasing CO_2 conversion when the GHSV is increased from 10000 to 15000 h^{-1}, which is in line with short reactant contact time. The impact is more pronounced at low temperature of 300 °C, but at high temperature of 400 °C, the conversion is almost comparable irrespective of GHSV. Experimental results indicate that Ni/Al_2O_3 gives the highest CO_2 conversion of 74% while 7% and 67% for Ni/ZrO_2 and Ni/La_2O_3 respectively. There is a prospect for further scaling up to complement the current commercial catalyst proven for handling low concentration of CO_2.

Keywords: *CO_2 Conversion; CO_2 Methanation; CO_2 hydrogenation; Nickel Catalyst*

1. Introduction

The increase of CO_2 concentration in atmosphere plays a key role in a climate change. New ideas and new technologies are required to control CO_2 emissions and this is a challenging task to be done. Chemical conversion of CO and CO_2 into added value products is one of the research area that is highly involved by scientists and industrialists.

Carbon dioxide (CO_2) can be used as either a technological fluid for building complex molecules block or a raw material in chemical processes as a carbon source for fuels or in biotechnological applications [1]. Currently, the utilization of CO_2 as chemical feedstock is limited to a few processes such as synthesis of urea (for nitrogen fertilizers and plastics), salicylic acid (a pharmaceutical ingredient), and polycarbonates (for plastics) [2]. Methane, a feasible chemical energy carrier that can easily be stored, transported and converted into energy while solely employing existing infrastructure and technology. A physical-chemical process which converted CO and CO_2 into CH_4 is called methanation. A sufficient supply of hydrogen is necessary for such conversion, which can be obtained from industries with excess hydrogen or generated by water electrolysis and some kind of renewable energy [3].

The methanation process, also called Sabatier reaction, has been known since the beginning of the 20th century. This process is highly exothermic and proceeds as Eq. 1:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad (1)$$

$$\Delta H_R = -165 \text{ kJ/mol} \qquad \Delta G_R = -114 \text{ kJ/mol}$$

This reaction is favored at lower temperatures, however due to kinetic limitations, a catalyst need to be utilized [4]. The reaction between CO_2 and hydrogen over heterogeneous catalysts is an issue that has received a great appreciation because of its possibility to manufacture and substitute natural gas, reducing thereby the price of gas obtained from coal. The catalysts investigated for CO_2 methanation are generally made up of Group 8 (Fe, Ru, Os), 9 (Co, Rh, Ir), 10 (Ni, Pd, Pt) and 11 (Cu, Ag, Au) transitions metal. CO_2 methanation requires high-energy substances and entails an eight-electron process with kinetic limitations because the highly oxidized CO_2 molecule is highly thermodynamically stable, which makes this compound not reactive [5,6].

Various catalysts have been developed for the promotion of CO_2 methanation. The well-known metal catalysts for this reaction are Ru, Rh, Pd and Ni [7]. These metal catalysts are supported on metal oxides (e.g. Al_2O_3, SiO_2, zeolites, TiO_2, CeO_2 and CeO_2-ZrO_2) [8,9]. The different types of defects and environments (kinks, steps, terraces) of an oxide surface contribute to the catalytic phenomenon [10]. Study has found that the precious metal catalysts possess better activity than Ni whereby the formation of CH_4 at room temperature and atmospheric pressure over Ru/TiO_2 catalyst [11]. However, they are not suitable for the industrial application due to their high cost. Thus, Ni based catalysts are the most common studied for CO_2 methanation because of their high activity and low price.

A catalyst with high selectivity, activity and stability is essential in the chemical processing industry. In order to meet these requirements, the catalyst support should provide sufficient surface area, stability and to be composed of a robust material for a high dispersion of the metal [12]. Mesoporous alumina or silica has been reported to exhibit variable performances in terms of selectivity and activity for methanation process and this support can be one of the potential candidates for Ni catalysts. Previous study shown that the high activity of Ni/alumina was correlated to the existence of both intra and inter particle porosity and to the high basicity of the catalysts which led to the high Ni dispersion on the surface of support [13,14].

This paper focused on Ni catalysts supported on various metal oxides for CO_2 methanation, carrying out the process at 300 to 400 °C and atmospheric pressure. We aimed to investigate the methanation performances due to the optimization of different reaction parameters as it was expected to give promising results.

2. Experimental Methodology

2.1 Sample preparation

Nickel catalysts supported on metal oxides were prepared by wet impregnation method at room temperature. Nickel (II) Nitrate Hexahydrate, with a chemical formula of $Ni(NO_3)_2.6H_2O$, supplied by Sigma Aldrich was used as the base in this research. Meanwhile, the following oxides were employed as support materials: Aluminum Oxide 98% Al_2O_3 basis (Sigma Aldrich), Zirconium (IV) Oxide 99% trace metal basis (Sigma Aldrich) and Lanthanum Nitrate Hexahydrate (Fluka). The $Ni(NO_3)_2.6H_2O$ salt solution was slow and steadily added to the supports in the form of solid oxide while stirring. The solution was allowed to stir continuously. The solution was then evaporated to dryness to remove the excess water. The catalyst precursors were then grinded to powder. The resulting powder was calcined at 500 °C for 4 hr in air.

2.2 Characterization

XRD patterns were obtained on a Bruker D8 Avance diffractometer, equipped with theta/2theta goniometer and a Scintillation counter detector. The patterns were recorded in reflection geometry in the range of $10° \leq 2\Theta \leq 80°$ with a step size of $\Delta 2\Theta = 0.02$. The specific surface area of each catalyst was evaluated by the BET method using N_2 adsorption-desorption (Micrometrics Tristar II). The samples were degassed for 5h at 200°C before the analysis. The surface area was calculated by BET method. Pore size distribution and pore volume were estimated using the Barret-Joyner-Halenda (BJH) model. The reduction of active metal oxide was evaluated by Temperature Programmed Reduction (TPR) in a H_2 flow system (Thermo Finnigan 1100). In a gas stream of $5\%H_2/N_2$, the samples were heated from 40°C to 900°C at heating rate of 10°C min^{-1}. The basic property of the sample was examined by NH_3 Temperature Programmed Desorption (NH_3-TPD). After pre-treatment at 120°C for 1h under He, $10\%NH_3/He$ was supplied to saturate the catalysts at 50°C for 1h and followed by the flow of He to remove weakly physisorbed NH_3. The TCD profiles of the chemisorbed NH_3 were obtained by heating the sample from 50 to 500°C at a heating rate 10°C min^{-1} under He flow.

2.3 Catalytic Activity

The prepared catalysts were pelletized and pulverized prior to evaluation. The catalytic reaction was performed in a fixed-bed reactor under atmospheric pressure. The precursors were reduced with H_2 gas at a flow rate of 20 ml.min^{-1} before the reaction. The process block diagram is shown in Figure 1. As can be seen in the figure, the reaction system comprising three units which are a feeding unit, a reaction unit and a product gas analysis unit.

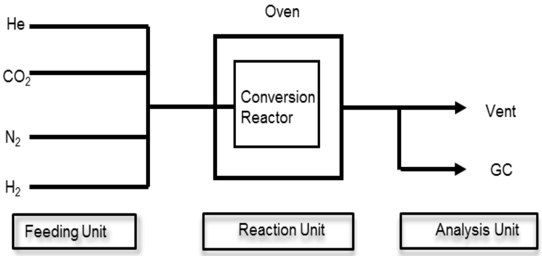


Fig. 1: Process block diagram of catalytic reactor system

After the catalysts were activated, the reactors were heated to the working temperature ranging from 300 to 400°C under atmospheric pressure with a supply of feed gases of (H_2:CO_2) with ratio 4:1. The gas hourly space velocity (GHSV) was varied between 10,000 and 15,000 h^{-1}. The composition outlet gas was analyzed by an online gas chromatograph with a thermal conductivity detector. Conversion of CO_2 (X_{CO2}) and CH_4 selectivity (S_{CH4}) were calculated according to equations (2) and (3):

$$X_{CO2}(\%) = (F_{CO2,in} - F_{CO2,out})/F_{CO2,in} \text{ x } 100 \quad (2)$$

$$S_{CH4}(\%) = F_{CH4,out}/(F_{CH4\,out} + F_{CO2,out} + F_{C,out}) \text{ x } 100 \quad (3)$$

where F denote the flow rate (ml.min^{-1}) of the component at the inlet and outlet.

3. Results and discussion

The XRD structural properties of the synthesized catalysts were first investigated by X-ray diffraction measurement as illustrated in Figure 2. The crystal structure of the samples was examined before and after calcination. The supported Nickel catalysts showed the diffraction peaks corresponding to NiO species and phases, Al_2O_3, ZrO_2, and La_2O_3. The reflections at 2Θ of of 43.3°, 42.9° and 37.3° confirm the presence of nickel oxide to the (200) and (111) planes which can be observed this peaks in Figure 2 (a) and (b). However, signature peaks of nickel oxide were not observed for Ni/La_2O_3 catalyst. This result suggested that the incorporation of nickel onto the surface of lanthanum oxide altered the phase which the composite of lanthanum nickel oxide might formed [15].

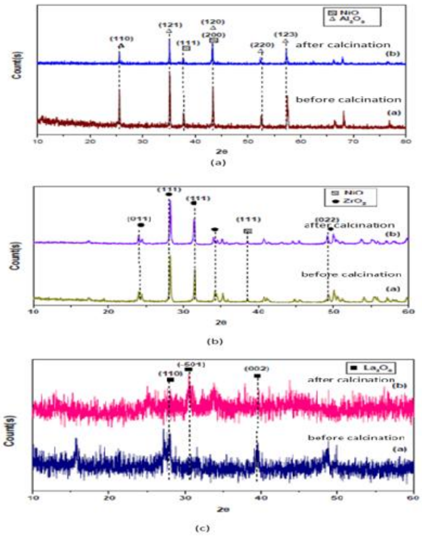


Fig. 2: XRD patterns of Ni/metal oxide catalysts (a) Ni/Al_2O_3 (b) Ni/ZrO_2 (c) Ni/La_2O_3

Surface area and porous structure of the synthesized supported metal oxide catalysts were studied by the BET method. The N_2 adsorption-desorption isotherms of all Ni supported catalysts exhibit reversible Type II isotherm (Figure 3) representing unrestricted monolayer-multilayer adsorption according to IUPAC classification [16]. These isotherms with H2-type hysteresis loops, indicated a typical hysteresis for mesoporous materials. Pore diameter for all synthesized supported metal oxide catalysts is between 2-50 nm which exhibits the material is mesoporous proven by the hysteresis loops. These demonstrated that accessible path for CO_2 molecules to the active sites within the catalyst pores thus making supported Nickel catalysts a potential candidate for CO_2 methanation. Table 1 summarized the BET results for supported Ni catalysts.

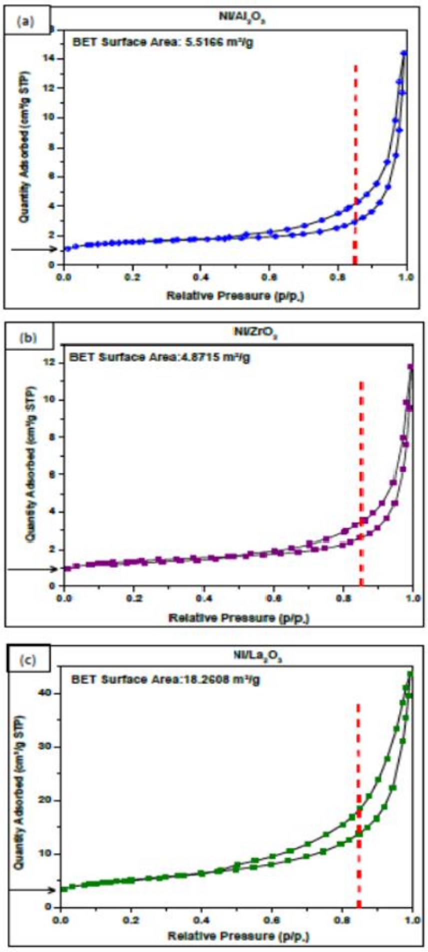


Fig. 3: N_2 adsorption-desorption isotherms of supported Ni based catalyst (a) Ni/Al_2O_3, (b) Ni/ZrO_2, (c) Ni/La_2O_3

Table 1: Physicochemical properties of supported Nickel catalyst

Catalyst type	**S_{BET} (m^2/g)**	**Pore Volume (cm^3/g)**	**Average Pore Diameter (nm)**
Ni/Al_2O_3	5.5166	0.021769	21.7067
Ni/ZrO_2	4.8715	0.018083	20.1239
Ni/La_2O_3	18.2608	0.067980	13.1603

Surface area which is indirectly representing active sites location is important to benefit from reactants/products sorption sites and active sites positioning, however they can only perform when reactants and products have accessibility to diffuse in/adsorb-diffuse out/desorb. Thus properties have a big and direct influence on catalytic activity. BET results from Table 1 showed that, Ni/Al_2O_3 has a small surface area as compared to Ni/La_2O_3. However, its larger pore diameter as compared to Ni/La_2O_3 makes the available active sites highly accessible for adsorption hence increased catalytic activity. The large surface area measured from Lanthanum Nitrate Hexahydrate used might not necessarily reflect the Ni active site, thus implying that reactions took place on the external surface of the catalyst support.

The H_2-TPR profiles of the Ni catalysts are shown in Figure 4. The end temperature was taken as the reduction temperature for in-situ reduction in the reactor prior to catalyst screening to ensure the active component oxides was fully reduced. Most of the Ni species in Ni/Al_2O_3, Ni/ZrO_2 and Ni/La_2O_3 catalysts were reduced up to 500°C, indicating that the Ni species was in the metallic state at the beginning of activity test. However, the TPR profile of Ni/La_2O_3 shows another distinct hump at 600°C which maybe the reducing temperature of Lanthanum Oxide (La_2O_3). The presence of La also shifted the Ni^{2+} reduction peak to a slightly lower temperature from 400°C to 350°C, but appeared to suppress the reduction of Ni^{+} to Ni^{0} metal, perhaps due to the formation of mixed nickel lanthanum oxide which deduced from TGA analysis which was harder to be reduced [17].

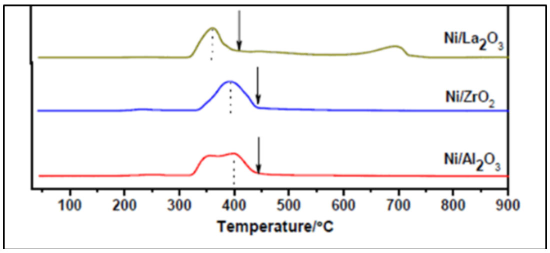


Fig. 4: H_2-TPR profiles of Ni/metal oxide catalysts

Figure 5 shows the NH_3 desorption behavior of the Ni catalysts. The peak in the high and low temperature zone can be attributed to desorption of NH_3 from the strong and weak acid sites. Above 700°C, the peak observed can be due to the desorption of NH_3 from strong Brønsted acid site while peaks below 360°C may be attributed to the desorption of NH_3 from weak acid sites [18]. Ni/Al_2O_3, and Ni/ZrO_2 catalysts gave a small desorption peak at 245°C and 273°C which indicates a weak acid strength. However, these two catalysts together with Ni/La_2O_3 also have desorption peak above 400°C which attributes to a moderate acid strength.

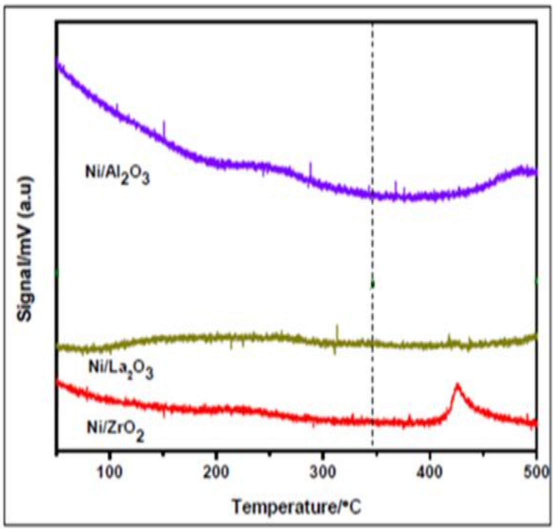
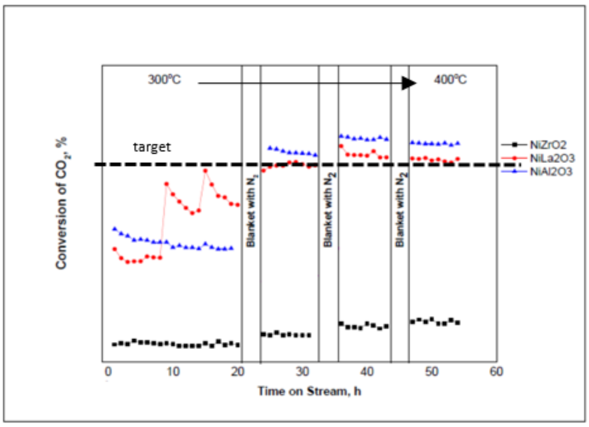
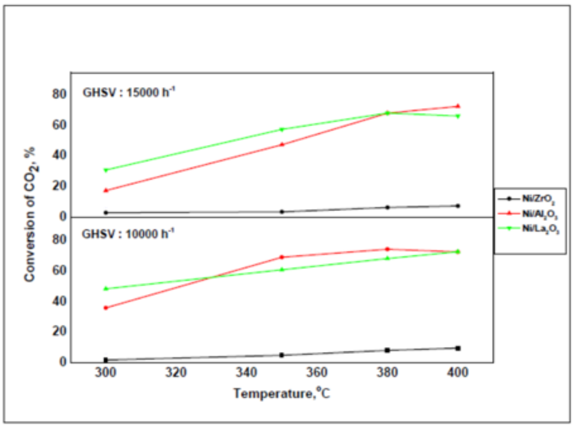


Fig.5: NH_3-TPD profiles of Ni/metal oxide catalysts

Concerning the catalytic activity results, the catalytic performance of oxides-supported nickel catalysts were evaluated in the gaseous phase hydrogenation of CO_2. Figure 6 summarizes the performances of these catalysts in CO_2 conversion screening at different temperature and GHSV.



(a)



(b)

Fig. 6: (a) Conversion of CO_2 over Ni/metal oxide catalysts at different temperature (b) Conversion of CO_2 over Ni/metal oxide catalysts at different GHSV

Figure 6(a) presents the catalytic activity at temperature ranging from 300 to 400°C at GHSV 10,000 h^{-1}. As temperature increased, all catalysts started increasing their catalytic activity. The CO_2 conversion was very low for Ni/ZrO_2 at 2%. CO_2 conversion increased when the temperature increased [12], towards 400°C ending up at 7% for Ni/ZrO_2, 67% for Ni/La_2O_3 and 72% for Ni/Al_2O_3. These results indicate that optimum working temperature for both Ni/La_2O_3 and Ni/Al_2O_3 is at 380°C whereas Ni/ZrO_2 shows optimum working at high temperature, 400°C . Among these catalysts, it is observed that Ni/Al_2O_3 gives better performance compare to other catalyst with 74% CO_2 conversion.

Figure 6(b) shows the impact of space velocity on CO_2 conversion for the Ni/metal oxides catalysts. As expected, the activity lowers by increasing the GHSV from 10,000 h^{-1} to 15,000 h^{-1}. This suggest that short reactant contact time with catalyst represented by high GHSV would give low conversion. The impact is more pronounced at low temperature of 300°C, but at high temperature of 400°C, the conversion is almost comparable irrespective of GHSV.

The methanation process takes place in the presence of all the catalysts. This can be noticed from Figure 7. The graph shows selectivity of CH_4 at GHSV 10000h^{-1} at temperature ranging from 300 to 400°C. The highest CH_4 selectivity was achieved at 380°C on the Ni/Al_2O_3 catalyst at 80%. This reflect to the highest CO_2 conversion in Figure 6. Methane formation appears to be limited by the dissociation of carbon dioxide to carbon species which further react with hydrogen to

produce methane and it is observed to be related to the high activity of Ni/Al_2O_3 [11].

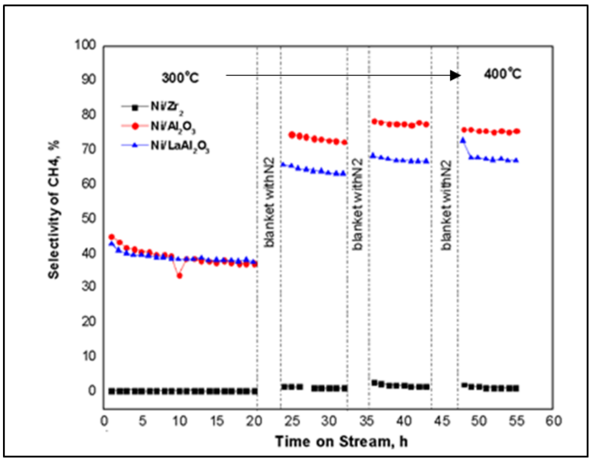


Fig. 7: Selectivity of CH_4 over Ni/metal oxide catalysts at 10000 h^{-1} GHSV

4. Conclusion

In summary, Ni/Al_2O_3 was determined to be the most active catalyst for CO_2 methanation among other metal oxide supports studied, in this case ZrO_2 and La_2O_3. The larger pore diameter of Al_2O_3 makes the available active sites highly accessible for adsorption hence increased catalytic activity. The exceptional values for selectivity (80%) was obtained at moderate hydrogenation conditions from the perspective of methane synthesis using low cost metal catalyst.

This study justifies the opportunity and possibility of using Ni/metal oxide catalyst, Ni/Al_2O_3 to be specific. This CO_2 hydrogenation route appears attractive for further economic evaluation.

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